

## **OIL SPILL BEHAVIOUR AND MODELING \***

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### **ABSTRACT**

The behaviour of oil in the environment is reviewed. This is then applied to modeling of the behaviour of oil in the environment once spilled. The most important behaviour of oil in terms of modeling its fate when spilled is evaporation. Significant numbers of modeling equations are available. The second most important behaviour aspect of oil is the formation of water-in-oil emulsions.

Natural dispersion of oil is the next most important factor. Oils which contain large fractions of small saturates will disperse naturally given high sea energies. Modeling equations for this factor are primitive. A related factor, dissolution, is not as important in terms of mass balance but is important in terms of toxicity in the environment. Laboratory work shows that the dissolution of oils can be predicted and measured, but no models incorporate dissolution as a separate term from dispersion.

There are several lesser chemical and behaviour aspects to oil, these include photooxidation, sinking and biodegradation.

### **1.0 INTRODUCTION**

Fate and behaviour studies are fundamental to oil spill modelling and their results are important for operational response. Knowledge of the ultimate fate and behaviour of oil should drive countermeasures decisions.

The state-of-the-art in the field of fate, behaviour, weathering, and modelling could be summarized as variable. There are many deficiencies in our knowledge about the fate, weathering, and modelling of oil spills.

The fate, behaviour, and transformation of oil are dominated by the reality that oil is a varying mixture of hundreds of compounds. Many laws of chemistry and physics are inapplicable to oil because they assume ideal liquid or gas behaviour. Much of the knowledge possessed by chemists is difficult to apply to the field. Examples of this include even standard physical measurements such as pour point. Oil, strictly speaking,

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does not have a single boiling point, a melting point, nor an evaporation rate. The components of oil have their own well defined physical parameters, but these are modified and obscured by the bulk behaviour factors. In the place of these 'pure' chemical parameters, we have developed bulk parameters to describe oil properties and behaviour. The bulk components of oil include the saturates, aromatics, resins and asphaltenes. The behaviour of oil can be related to the content of these components.

## 2.0 BEHAVIORAL ASPECTS

The behaviour of oil in the environment is largely dictated by its chemical composition. The behaviour of oil might be best summarized by examining several specific groups of oils. Fuels such as gasoline or diesel fuel are most influenced by evaporation in the environment. Gasoline in warm climates will be 90% evaporated on water within about one day and in about two days in cold circumstances. Both gasoline and diesel fuel will disperse naturally to a large degree in turbulent waters. Diesel fuel will evaporate to the extent of about 60% (percentage lost) in about 3 days on warm water and in 6 days on very cold waters. A light crude oil will evaporate to about 40% in about two days and will disperse naturally (depending very much on saturate content) in turbulent seas. After evaporation it may form water-in-oil emulsions, depending on asphaltene, resin and aromatic content. Medium crudes rarely disperse naturally to any great extent. A heavy crude will evaporate to about 15% (loss) and will almost never disperse naturally. Heavier crudes usually have a large percentage of asphaltenes and resins and will, after some evaporation, often form water-in-oil emulsions. Residual oils, such as Bunker C, will only lose about 4% of their volume to evaporation after two days. Bunker C may have a higher volume of asphaltenes and a lower content of aromatics and thus can form emulsions. Bunker C will not disperse naturally to any extent because it has little light saturate content.

The most important behavioural aspect is felt to be evaporation. Evaporation is responsible for the largest mass balance change in oils except for those rare times when oils disperse naturally. Evaporation is generally necessary before emulsification occurs and is a competing process to natural dispersion. It is then appropriate to discuss evaporation first. The second most important factor is felt to be emulsification. This is because, if emulsification occurs, it changes the spill dynamics and behaviour to a large degree. The viscosity of the resulting product is 1000 times the starting viscosity, the spilled product is now 5 times the volume of the starting spill volume, and spreading and evaporation nearly cease. The third factor, natural dispersion, or loss to the water column in the form of small droplets is an important phenomenon. Oil spills where a high-saturate oil is involved in a turbulent sea, can be dispersed totally, a case in point is the BRAER spill in the Shetlands. Other oils as noted above will disperse to little degree. Dissolution is a fourth behavioural phenomenon, although never greater than 1% of the oil, it is important for the toxicity of the oil to aquatic life. Finally there are other phenomena, such as photooxidation, sinking and biodegradation which are less important in terms of the oils overall mass balance.

## 2.1 EVAPORATION

Evaporation is the most important change that most oil spills undergo. Although the process of evaporation of crude oils is understood, the application of evaporation equations in spill models is sometimes difficult. This relates to the input data required to make many of the equations operative. The most commonly used in the past was that of evaporative exposure as proposed by Mackay and Matsugu (1976). Fingas (1995a) showed that oil evaporation is not the same as water evaporation and developed a series of simple equations that can predict evaporation amount.

## 2.2 EMULSIFICATION

Emulsification is the process of the formation of water-in-oil emulsions often called "chocolate mousse" or "mousse" among oil spill workers. These emulsions change the properties and characteristics of oil spills to a very large degree. Stable emulsions contain between 50 and 80% water thus expanding the volume of spilled material from two to five times the original volume. Most significantly, the viscosity of the oil typically changes from a few hundred cSt (Centistokes, a common unit of viscosity) to about one hundred thousand cSt, a typical increase of 1000. This changes a liquid product to a heavy, semi-solid material. Emulsification is felt by many to be the second most important behavioural characteristic after evaporation. Emulsification has a very large effect on the behaviour of oil spills at sea. As a result of emulsification, evaporation slows by orders-of-magnitude, spreading slows by similar rates. Emulsification also has significant effects on other spill aspects; spill countermeasures are quite different for emulsions. Emulsions are hard to recover mechanically, treat or burn.

The literature shows that there is some understanding of the formation of water-in-oil emulsions. Information on the kinetics of formation at sea and other modelling data is less abundant. Emulsion formation is a result of surfactant-like behaviour of the polar and asphaltene compounds. These are similar compounds and both behave like surfactants when they are not in solution. When there are insufficient amounts of aromatic components to solubilize the asphaltenes and polars, these precipitate and are available to stabilize water droplets in the oil mass. The minimum mass percentage of either asphaltenes or resins to stabilize an emulsion is about 3%. Emulsions begin to form when the above chemical conditions are true and when there is sufficient sea energy. The rate of emulsion formation was investigated in some laboratory studies and was found to be first-order with time. This can be approximated with a logarithmic (or exponential) curve (Fingas et al., 1995b, 1996)

Little work on modelling of emulsion formation has been done. Most models that incorporate the phenomenon use the Mackay and co-workers (1980) estimation technique or a variation of this.

### 2.3 NATURAL DISPERSION

Natural dispersion is the movement of droplets in the size range of 1 to 50 microns into the water. This is without the addition of chemical dispersing agents or chemical dispersion. Natural dispersion is sometimes grouped with the temporary transport of very large droplets (> 50 microns) and dissolution. This is often termed entrainment. Empirical equations to characterize this phenomenon were developed by Delvigne and Sweeney (1988) using a wave tank. The difficulties with this type of approach are that the predictions of entrainment are typically excessive (often 50% is predicted to go into the water column versus an actual percentage far less than 1%); this process groups all three phenomenon of dispersion, macro-droplet transfer and dissolution into one process, and finally the process is usually hinged to the amount of white-caps present on the ocean. The latter is known to be a poor indicator of sea energy and dispersion is known to occur without the presence of any white caps.

Studies into the natural dispersion of oil have shown that dispersion only occurs with the saturate fraction of oil and that the presence of significant amounts of asphaltenes retards this process (Fingas *et al.*, 1993). The amount of dispersion increases with increasing turbulent energy, a parameter which is very difficult to measure.

### 2.4 DISSOLUTION

Dissolution accounts for only a small portion of oil loss but is still considered to be a very important behaviour parameter. This is because the soluble components of oil - particularly the smaller aromatic compounds, are toxic to aquatic species. Most models in existence do not separate the dissolution component. The entrainment model as noted above is sometimes used, but fails to distinguish between dispersion and dissolution.

Only a small portion of oils are truly soluble in water. The solubility varies from 1 to about 100 ppm. The oil-to-water ratio is important in the total solubility. At sea this is expected to be a large ratio and thus the total solubility is low. The solubility for a fuel can be as large as 100 ppm and that for Bunker C less than 1 ppm. This represents very low loss rates for the fuel and for modelling purposes is not significant or relevant. The process of solubilization appears to be very rapid and based on laboratory data would be complete after about 15 minutes of contact with water. This data could be used directly to predict the source strength of the dissolved components.

### 2.5 PHOTOOXIDATION, SINKING AND BIODEGRADATION

Photooxidation is the transformation of some chemical components of the oil into polar components by the addition of oxygen. This essentially increases the resinic and to a lesser degree, asphaltenic components of the oil. It is important only in that as photooxidation increases so too does the potential for emulsion formation. Environment Canada studied a number of oils and found that oils vary widely in their susceptibility to photooxidation. There is a significant knowledge gap in being able to predict the degree of photooxidation and the extent that this would influence emulsification.

Sinking of oil can be divided into two phenomena, sedimentation of oil droplets and sinking *en masse*. The latter can be further divided into over-washing by water and simple sinking. All phenomena are not well understood in terms of prediction capability in models. Sinking *en masse* has been studied by a number of workers. Sedimentation has been studied, but the results have varied from a significant effect (40% sedimented to no effect).

Biodegradation is a very slow process that changes the behaviour and fate of oil spills to only a very small degree (Atlas and Bartha, 1992). For this reason, few modellers include the phenomena in their models.

### 3.0 CONCLUSIONS

The behaviour of oil spills is dominated by the chemistry or composition of oil. The composition can be simplified by measuring the group components of saturates, aromatics, asphaltenes and resins. The most important behavioural aspect of oil spills is their evaporation. Evaporation generally causes the largest changes in mass balance after the spill and influences other behavioural parameters. Emulsification is the second-most important aspect. Oils that emulsify undergo a rapid increase in viscosity, typically 1000 times, and nearly cease spreading and evaporating. Emulsification is dependant on oil composition, resins and asphaltenes stabilize water in the emulsion; aromatics dissolve the asphaltenes and thus delay emulsification. Some oils can lose sufficient aromatics by evaporation to emulsify. Natural dispersion is the third-most important behaviour displayed by spilled oils. The saturate component of oils disperse in highly turbulent situations. Asphaltenes are a deterrent to natural dispersion.

The behavioural aspects of oil spill are generally poorly-studied and even more poorly modelled. Most data are empirically-derived with a generous portion of assumptions thrown in. Evaporation is probably the best understood and modelled behaviour. Emulsification is somewhat understood but poor models currently exist. Natural dispersion is poorly understood and modelled.

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